A SECOND LOOK AT THE REDUCTIVE ALKYLATION OF COAL

AND AT THE NATURE OF ASPHALTENES

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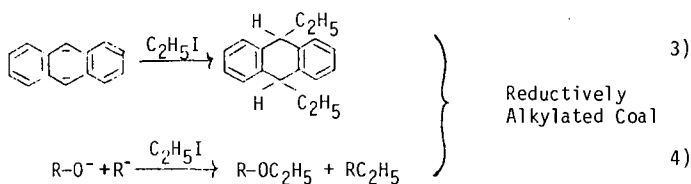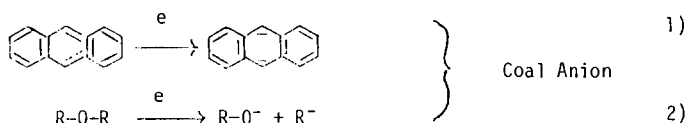University of California
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I am greatly honored to receive the 1976 Storch Award. It seems that I am the beneficiary of Dr. Storch's achievements on two counts: first as the recipient of the Award established as a memorial to him, and second for having the good fortune to work in the research environment created by Dr. Storch and continued by his successors.

I would like to take this opportunity to update our work on the reductive alkylation of coal and on the nature of asphaltenes. During the past two years I have had occasion to present these topics in formal and informal talks and to benefit from questions raised and criticisms offered. The purpose of this paper is to deal with some of these questions and to suggest further work in these areas of coal research.

Reductive Alkylation of Coal

Reductive alkylation of coal (1,2) involves essentially four types of reactions:

1. Addition of electrons to the aromatic hydrocarbon structures of coal (illustrated by anthracene) to form the corresponding aromatic hydrocarbon anions.

2. Cleavage of ether bonds to form the corresponding phenolate anions.

3. C-alkylation of the aromatic hydrocarbon anions.

4. O-alkylation of the phenolate anions.

$$R-O-R \xrightarrow{\ e\ } R-O^- + R^-$$

Coal Anion — 1), 2)

$$R-O^- + R^- \xrightarrow{C_2H_5I} R-OC_2H_5 + RC_2H_5$$

Reductively Alkylated Coal — 3), 4)

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The products formed according to equations 1 and 2 represent the coal anion, those formed according to equations 3 and 4, the reductively alkylated coal. It must be emphasized that hydroxylated aromatic compounds such as naphthol or anthranol do not undergo C-alkylation. The negative charge in the anion Ar-O$^-$ is partially distributed over the aromatic ring and thereby prevents further addition of electrons to the latter. Reductive alkylation of aromatic hydrocarbons in coal can take place only when these aromatic hydrocarbons are separated from aromatic hydroxy compounds by sp^3 carbons or other linkages that do not transmit resonance effects. Reductive alkylation of Ar-O$^-$ anions may take place if the aromatic ring system, Ar, is large enough to accommodate two or more negative charges.

Effect of Alkali Metal on the
Reductive Alkylation of Coal

A criticism often voiced with regard to the mechanism (equations 1-4) proposed for the reductive alkylation of coal runs along the following lines.

Reductive alkylation of coal probably involves a variety of reactions including free radical and elimination reactions. For example, reductive alkylation removes about half of the sulfur and one third of the nitrogen present in the untreated coal (1,2). Removal of sulfur is probably due to conversion of dibenzothiophene structures to biphenyl ring structures with elimination of sulfur as H$_2$S (3). In a similar way, removal of nitrogen may be due to conversion of carbazole to biphenyl ring structures with elimination of nitrogen as NH$_3$ (4). It might be misleading therefore, to assume that only the reactions described by equations 1-4 are taking place during reductive alkylation of coal.
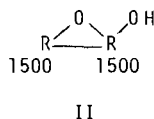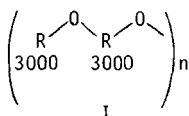
Though this criticism is justified, we must not lose sight of the fact that, on the whole, equations 1-4 accurately describe the main reactions that are taking place during reductive alkylation of coal. A good indication that C-alkylation of aromatic hydrocarbon anions plays a major role is the effect of alkali on the extent of alkylation. In the presence of lithium, 7.2, while in the presence of potassium, 8.8 alkyl groups per 100 carbon atoms are added to the coal anion (1).

At the time we reported this result (1) we had no explanation as to why potassium should be more effective than lithium. Since then we have learned that a similar effect was observed and reported by P. W. Rabideau and R. G. Harvey in a paper entitled "A Novel Metal Effect in the Reductive Methylation of Naphthalene" (5). These authors found that methylation of naphthalene in liquid ammonia in the presence of lithium yielded predominantly the monomethyl while methylation in the presence of sodium produced the dimethyl derivative as the major product. The authors attributed this difference to the fact that the lithium-naphthalene ion pair exists as a solvent separated ion pair, while the sodium-naphthalene ion pair is present as an intimate (contact) ion pair. Now the naphthalene anion in the sodium-naphthalene ion pair is less susceptible to protonation by the solvent than the naphthalene anion in the lithium-naphthalene ion pair. Consequently, the naphthalene anion in the sodium ion pair adds two methyl groups while the napthalene anion in the lithium ion pair, being more susceptible to protonation, adds one proton and one methyl group. In applying these results to coal, one could say that the coal (aromatic hydrocarbon) anion in the potassium-coal ion pair is less susceptible to proton attack than the coal anion in the lithium-coal ion pair. Consequently the former is more extensively alkylated than the latter.

Ether Cleavage vs. C-Alkylation

The following question is always raised in discussions on the conversion of coal to a benzene soluble product by reductive alkylation: Is the conversion of coal to a benzene soluble product due to C-alkylation (addition of alkyl groups to the aromatic hydrocarbon anions) or due to ether cleavage? I do not think that this question can be decided on the basis of experimental evidence available to date.

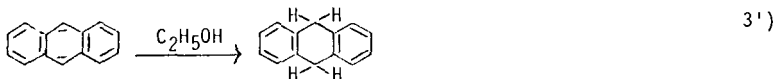To illustrate this point, we may consider two extreme coal structures, I and II.

$$\left(\begin{array}{c} R \diagup^{O} \diagdown R \diagup^{O} \diagdown \\ 3000 \quad\quad 3000 \end{array} \right)_n \qquad\qquad R \overset{O}{\diagup}\diagdown R \diagup^{OH} \\ 1500 \quad\quad 1500$$

$$ I II$$

In both cases, ether cleavage yields units with the same molecular weight, i.e. 3000:

$$I \xrightarrow[H_2O]{e} R \diagup^{OH} \atop 3000 \qquad\qquad\qquad\qquad 5)$$

$$II \xrightarrow[H_2O]{e} R \diagup^{OH} \!\!\!\!- R \diagup^{OH} \\ 1500 \quad 1500 \qquad\qquad\qquad 6)$$

Those who prefer structure I argue that without ether cleavage, C-alkylation could not impart benzene solubility either to the original coal or to the cleavage products. Those who prefer structure II believe that C-alkylation suffices to convert II into a benzene soluble product. In other words, if coal had a polymeric structure such as I, then C-alkylation would be necessary but not sufficient to convert coal into a benzene soluble product. Ether cleavage in addition to C-alkylation would be required to make coal, having a structure such as I, benzene soluble.
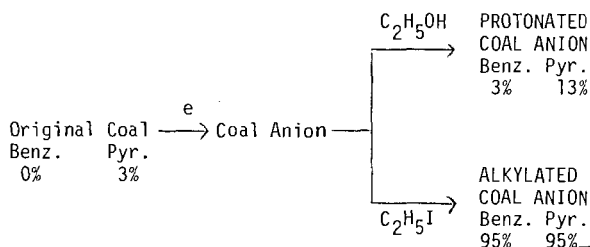
Though we do not know whether ether cleavage is necessary to convert coal into a benzene soluble product, there is experimental evidence (1) that ether cleavage alone is not sufficient. When coal is converted to the coal anion, ether cleavage takes place (equation 2) along with formation of aromatic hydrocarbon anions (equation 1). When the coal anion is now treated with a proton donor such as ethanol, protons are added to the anions to give the corresponding hydrocarbons and phenols according to equations 3' and 4' (analogous to equations 3 and 4).

$$\text{(naphthalene/anthracene)} \xrightarrow{C_2H_5OH} \text{(dihydro product)} \qquad\qquad 3')$$

$$R-O^- + R^- \xrightarrow{C_2H_5OH} R-OH + HR \qquad\qquad 4')$$

In contrast to the alkylated coal anion which was 95% soluble, the protonated coal anion was only 3% soluble in benzene. These results along with the benzene and pyridine solubilities of the starting coal and treated coals are summarized in Figure 1.

Figure 1

Benzene and Pyridine Solubility of Original and Treated Coals

$$
\begin{array}{ccc}
& & \xrightarrow{\;C_2H_5OH\;} &
\begin{array}{l}
\text{PROTONATED} \\
\text{COAL ANION} \\
\text{Benz. \ Pyr.} \\
\quad 3\% \qquad 13\%
\end{array} \\[2em]
\text{Original Coal} \xrightarrow{\;e\;} \text{Coal Anion} & \\
\begin{array}{l}\text{Benz.} \quad \text{Pyr.} \\ \; 0\% \qquad 3\% \end{array} & & \\[2em]
& & \xrightarrow{\;C_2H_5I\;} &
\begin{array}{l}
\text{ALKYLATED} \\
\text{COAL ANION} \\
\text{Benz. \ Pyr.} \\
\quad 95\% \quad 95\%
\end{array}
\end{array}
$$

From Figure 1 it seems that alkylation of the coal anion is necessary to convert coal to a benzene soluble product.

Ether Cleavage and Pyridine Solubility

When we first published our work on solubilization of coal by reductive alkylation we were primarily interested in the benzene solubility of the treated coal. Since then we have found (6,7) that pyridine soluble, benzene insoluble material is present in coal conversion products such as SYNTHOIL and solvent refined coal (SRC). In light of these findings, the increase in pyridine solubility indicated in Figure 1 assumes a new importance. This increase in pyridine solubility from 3% to 13% may not seem significant, but there is reason to believe that considerably higher pyridine solubilities may result if coals of higher oxygen content and lower molecular weight were subjected to ether cleavage. This prediction is based on the following considerations.

The increase in pyridine solubility of the protonated coal anion over the original coal (Figure 1) is probably due to depolymerization and/or increase in phenolic hydroxyl groups according to equations 5 and/or 6. Pyridine solubility will also be dependent on molecular weight, i.e., solubility will increase with decreasing molecular weight.
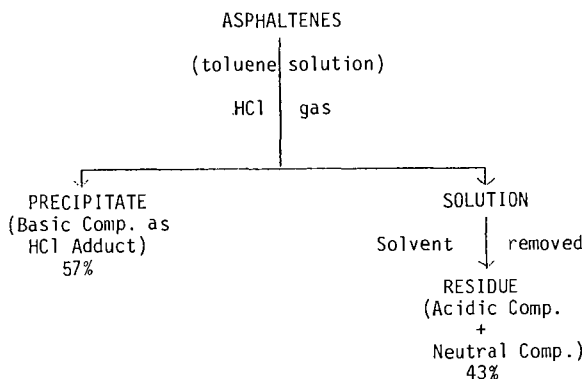
Now the experiments summarized in Figure 1 were carried out with Pocahontas coal, a coal of relatively high molecular weight of about 3000 (1) and low (3%) oxygen content. Recent work by J. Y. Sun and E. H. Burke (8) has shown that Southern Illinois coal with an oxygen content of 9%, i.e., three times that of Pocahontas coal has a molecular weight of only 770 or one fourth that of Pocahontas coal. It would be interesting to determine the effect of ether cleavage on pyridine solubility in Southern Illinois and similar coals of high oxygen content and low molecular weight. It is conceivable that ether cleavage may suffice to convert these coals into pyridine soluble products.

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Acid-Base Structure of
Coal-Derived Asphaltenes

Asphaltenes, operationally defined as material soluble in benzene and insoluble
in pentane, are key intermediates in conversion of bituminous coals to oil (9,10).
We found (11) that asphaltenes, isolated in 40% yield from a coal liquefaction
(SYNTHOIL) product, contained hydrogen bonded acid-base complexes and that these
complexes could be separated into their acidic and basic components indicated
in Figure 2.

Figure 2

Asphaltene Components

```
                          ASPHALTENES

                     (toluene solution)

                       HCl   gas
                              │
        ┌─────────────────────┴──────────────────────┐
        ↓                                             ↓
    PRECIPITATE                                    SOLUTION
    (Basic Comp. as
      HCl Adduct)                      Solvent  │  removed
        57%                                     ↓
                                             RESIDUE
                                          (Acidic Comp.
                                                +
                                           Neutral Comp.)
                                               43%
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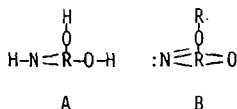
Based on ultimate analyses summarized in Table 1, and other experimental data (11),

Table 1

Ultimate Analyses and Molecular Weights of Asphaltenes
and Their Acidic and Basic Components

Material	Composition (%)						Molec- ular weight
	C	H	O	N	S	Cl	
Asphaltenes	87.43	6.52	3.52	2.16	0.37		417
Acidic component	87.40	7.04	3.39	0.99	0.51	0.67	550
Basic component (as HCl adduct)	83.35	5.78	3.48	2.72	0.53	4.14	
Basic component (calc. HCl-free)	87.06	5.91	3.64	2.84	0.55		368

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we arrived at the composite structures A and B for the acidic and basic compo-
nents:

$$H-N{\cong}\overset{\overset{\textstyle H}{|}\overset{\textstyle O}{}}{R}-O-H \qquad :N{\cong}\overset{\overset{\textstyle R.}{|}\overset{\textstyle O}{}}{R}{\cong}O$$

<div align="center">A   B</div>

The essential features of these structures may be summarized as follows. The
oxygen in the acidic component is present as phenolic hydroxyl and the nitrogen as
acidic nitrogen, as in pyrrole. The oxygen in the basic component is present as
ring or ether oxygen and the nitrogen as basic ring nitrogen as in pyridine. Complex
formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups.

It has been pointed out that inspection of Table 1 shows that the nitrogen
content (2.84%) of the basic component is too low to account for one nitrogen
per molecule of number average molecular weight of 368. Given a molecular weight
of 368 and assuming one nitrogen per molecule as indicated in the composite
structure B, the nitrogen content should be 3.95%. Our explanation is that the
low nitrogen content is due to the difficulties involved in determining nitrogen
in certain compounds (12). The standard Dumas method used for determining the
nitrogen content of the basic component may not have been adequate for this
purpose.

Acid-Base Structure of Coal

We suggested (11) that coal may have an acid-base structure analogous to
that of asphaltenes on the basis of the following considerations.

Our experimental data indicate that the acidic component contains all and
the basic component none of the acidic (deuterium exchangeable) hydrogen present.
This result precludes the possibility of the asphaltenes having an amphoteric
structure. That a complex mixture of compounds such as asphaltenes is composed
of acids and bases is an unexpected result. It suggests that coal, too, may have
an acid-base structure contrary to the generally accepted view that acidic and
basic functional groups are randomly distributed over the whole coal molecule.
It seems extremely unlikely that conversion of coal to asphaltenes could change
such a random distribution of acidic and basic functional groups into one where
these groups are segregated, that is, where acidic and basic functional groups
are attached to different molecules.

The acid-base structure of coal has been questioned. The objections and
replies may be summarized as follows.

1. Those who object to an acid-base structure point to the fact that there
are strict steric requirements as to bond lengths and bond angles for hydrogen
bonding to take place. It seems unlikely that such requirements could be met
by the large and complex structural units that are present in coal.

This objection is not necessarily valid. Complex hydrogen bonded structures are ubiquitous in biological material derived from plant and animal life. These hydrogen bonded structures, present at the start of the decay process, retain their hydrogen bonded configuration during coalification. There is no need to invoke any special rearrangements to explain the formation of these hydrogen bonds.

2. If the acidic and basic components in coal were held together only by hydrogen bonds, then it should be possible to break these bonds and to solubilize coal by treatment with polar solvents such as pyridine. Since this cannot be done, the acidic and basic components of coal must be linked by other bonds, probably covalent bonds.

This is a valid objection and must be taken into consideration when proposing coal structures containing acidic and basic components.

3. The extrapolation from asphaltene to coal structure is not justified in view of the fact that the asphaltenes represent only 40% of the liquified coal. These asphaltenes, it is argued, are clevage products and have a low molecular weight compared to that of the original coal. It is, therefore, not surprising that these relatively small units do not contain both acidic and basic functional groups. The situation may be entirely different for the large coal molecules which may contain both acidic and basic functional groups in the same molecule.

Perhaps some experimental evidence for or against this objection could be obtained by dissolving reductively alkylated coal in toluene and passing dry HCl gas through the solution as described in the case of the asphaltenes (Figure 2). Formation of an HCl-adduct and analysis of this adduct may answer the question as to whether large molecular weight basic components are present in coal. No acidic components would be present under these conditions since all of the phenolic hydroxyl groups would have been alkylated.

Coal Structure and the Conversion of
Coal to Pyridine Soluble Products

In the past it has often been tacitly assumed that the benzene insoluble material in coal conversion products consisted essentially of unreacted coal. We found (6,7) that this assumption is not justified. The benzene insoluble material is soluble in pyridine and soluble in the product oil where it exerts a large effect on viscosity. We assumed that this benzene insoluble, pyridine soluble material is intermediate between coal and benzene soluble, pentane insoluble asphaltenes; no longer coal and not yet asphaltenes. To differentiate the pyridine soluble, benzene insoluble material from the benzene soluble, pentane insoluble material we called the former "pre-asphaltenes" (7). It was recently found (13) that benzene insoluble, pyridine soluble material is formed in the presence of hydrogen donor solvents at elevated temperatures in solvent refined coal (SRC) processes, i.e. in the absence of an added catalyst. The contact time required for almost quantitative conversion of coal to pyridine soluble material is very short, of the order of minutes.

This pyridine soluble conversion product, is undoubtedly much closer related to coal than the benzene soluble, pentane insoluble asphaltenes. It will be interesting to determine whether it also contains acidic and basic components.

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In that case one could visualize coal structures where hydrogen bonded acidic and basic components are linked by covalent bonds as indicated in Figure 3. Similar structures have been suggested by Koelling and Hausigk (14).

Figure 3

Coal Structures

$$X= -(CH_2)_{\overline{n}} \, , \, -\overset{R}{\underset{}{C}}H- \, , \, -O- \, , \, -CH_2-O-$$
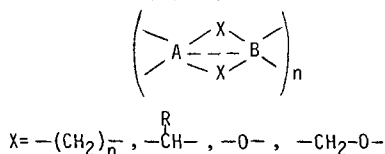
Work by Koelling and his coworkers (15,16) indicates that hydrogenolysis of coal may involve ether cleavage. They found that bituminous coal was converted in 1,2,3,4-tetrahydroquinoline at 300°C to a product 55% soluble in pyridine and having a molecular weight of 593. The authors attribute the solubilization of coal to cleavage of ether bonds on the basis of experiments with the following two groups of model compounds: (a) toluene, α-methylnaphthalene, diphenylmethane, diphenyl and (b) phenol, diphenylether, phenylbenzylether, dibenzylether. Treatment with tetrahydroquinoline at 390°C left the compounds in group (a) as well as phenol and diphenylether of group (b) unchanged. Phenylbenzylether and dibenzyl-ether, on the other hand, were quantitatively converted to phenol and toluene and to benzylalcohol and toluene respectively.

Evidence, based on the work of Heredy and Neuworth (17) indicates that the aromatic units in coal are linked by methylene bridges. In that case, conversion of coal to a pyridine soluble material by hydrogenolysis may be attributed to thermal cleavage of methylene C-C bonds followed by addition of hydrogen to the cleavage products.

Our work on the other hand, indicates that coal can be solubilized without breaking any C-C bonds and that cleavage of C-O ether bonds may be required to convert coal to a pyridine soluble product. On that view, conversion of coal to a pyridine soluble product by hydrogenolysis may be due to thermal cleavage of C-O ether bonds followed by addition of hydrogen to the cleavage products.

If conversion of coal to a pyridine soluble material is due to ether cleavage alone then electron addition followed by protonation (equation 7) should give the same product as hydrogenolysis in the presence of a donor solvent (equation 8).

$$R-O-R \xrightarrow[\text{Room Temp.}]{e,H_2O} R-OH + RH \qquad\qquad 7)$$

$$R-O-R \xrightarrow[400°C]{H-Donor} R-OH + RH \qquad\qquad 8)$$

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A comparison of pyridine soluble products obtained by reactions 7 and 8 should help answer the question whether or not cleavage of ether bonds is essential for the conversion of coal to a pyridine soluble material.

Conversion of coal to pyridine soluble material can be accomplished by phenol,BF_3 depolymerization (17), reductive alkylation (1,2) and hydrogenolysis in the presence of a hydrogen donor solvent (13). An investigation of the products obtained by these methods in conjunction with model compound experiments should lead to a better understanding both of coal structure and the mechanism of coal conversion.

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